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PLUMBOGUMMITE FROM SZŰZVÁR MINE, PÁTKA, (VELENCE MOUNTAINS, HUNGARY): FIRST OCCURRENCE IN HUNGARY

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ABSTRACT

Plumbogummite was found in the oxidation zone of the Szűzvár Mine, Pátka, Velence Mts., Hungary. The mineral forms crystallized crusts in fissures, intergrown with and overgrown by pyromorphite. Plumbogummite crystals are colourless to white or very pale brown. Microprobe analysis and the H_2O calculation leads to the structural formula $Pb_{1.08}Ca_{0.02}Al_{2.93}[(OH)_{6.29}|PO_3(OH)_{0.86}|PO_4]\times 0.98H_2O$. XRPD data confirm the identification of the mineral. This is the first occurrence of plumbogummite in Hungary.

Key words: plumbogummite, Velence Mts., Hungary, fluorite vein, oxidation zone, pyromorphite, alunite group minerals

INTRODUCTION

In this paper we report the first occurrence of plumbogummite from the oxidation-cementation zone of a fluorite-sulphide vein deposit, Szűzvár Mine, Pátka, Velence Mts., Hungary.

Plumbogummite was described by Romé de l'Isle in 1779 (Dana, 1892). Idealised formula: $PbAl_3[(PO_4)_2(OH)_5]\times H_2O$. Symmetry: ditrigonal pyramidal ($R3m$, a_0 = 7.033 Å, c_0 = 16.789 Å); a member of the crandallite-dussertite-florencite group with the alunite structure. Mohs hardness: 4.5, density: 4.025 g/cm^3. Morphological varieties: botryoidal, stalactitic, globular, crusts and masses with concentric structure, radially fibrous or spherulitic, rarely as crystals with hexagonal or pseudo-octahedral tabular outline. Lustre: vitreous, greasy, resinous, or dull (Slansky, 1977). Greyish white, yellowish-grey, brown, reddish brown (Fe), pale to deep blue (Cu). Streak: white. Chemically fairly resistant, insoluble in HF, but soluble in concentrated hot HNO_3. Optically uniaxial, but some part of the crystals can be anomalously biaxial (Slansky, 1977). Optically positive, ω = 1.653–1.680, ε = 1.675–1.698. (Data from Gaines et al., 1997, if not indicated otherwise.)

GEOLOGOCAL SETTING

The Velence Mts. are located in the central part of the Transdanubian region of Hungary. It is built up from post-collisional Variscan granite intruded into regional metamorphic shales, forming a contact metamorphic aureola around the intrusion (Buda, 1993). Different types of hydrothermal mineralizations occur in the Velence Mts.: 1, molybdenite bearing stockwork 2, pegmatite 3, polymetallic quartz-fluorite veins (Molnár, 1996). Polymetallic quartz-fluorite vein-type mineralizations were found in the Pátka, *Kőrakás Hill,* and the Pátka, *Szűzvár* areas. They are genetically related to the late hydrothermal stage of the Variscan endomagmatic activity.

In the Szűzvár area a 500 meter long and 1.2 meter thick, sulphide-quartz-fluorite vein crops out in a N–S strike direction, dipping eastward (Kiss, 1954; Jantsky, 1966). The vein was mined for fluorite between 1951 and 1967. The mineralization of the sulphide-quartz-fluorite vein was divided into two groups by Kiss (1954). The main part of the vein consisted of massive brecciated fluorite (from 5% up to 95%). The southern, smaller part of the vein was composed of rhythmically precipitated quartz, sphalerite, galena, chalcopyrite and a subordinate amount of fahlores (tennantite >> tetrahedrite). The primary phases of the mineralization were partially leached out by fluids, leaving vugs in the vein quartz. These cavities were filled by secondary minerals, like pyromorphite, cerussite (Kiss, 1954; Koch, 1985) and wulfenite (Tibor Nagy personal communication). This association could be related to a late hydrothermal phase. Plumbogummite was discovered in this association.

SAMPLING

Samples were collected from the dumps of the abandoned Szűzvár Mine, Pátka in 1996 and 1997. There is no direct information, about which part of the vein are the samples originated from, but the associated minerals indicate that the plumbogummite-bearing samples came from the sulphide-quartz variety of the composite vein. This type of the vein was restricted only to the southern part of the mine at the 35 m and 75 m levels (see in Jantsky, 1966).

ANALYTICAL METHODS

Reflected light microscopy and microphotometry were performed on a Zeiss MPM 400 unit at the Department of Mineralogy, Eötvös Loránd University.

SEM images were taken on an AMRAY 1830i/T6 scanning electron microscope operated at 20kV acceleration voltage at the Department of Metallurgy of the University of Miskolc.

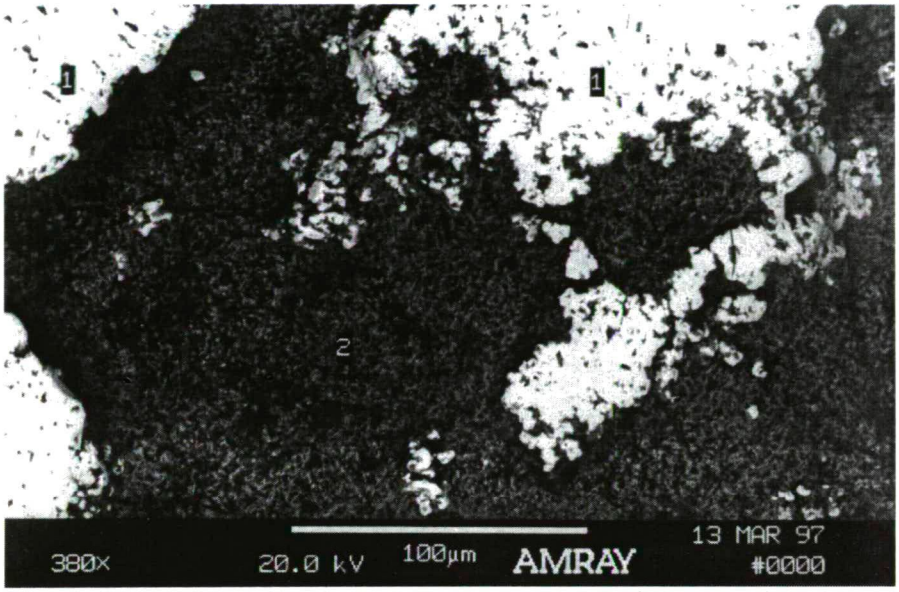

Fig. 1. Microgranular plumbogummite mass (grey) and pyromorphite (white) (back scattered electron (BSE) image). 1 = pyromorphite, 2 = plumbogummite.

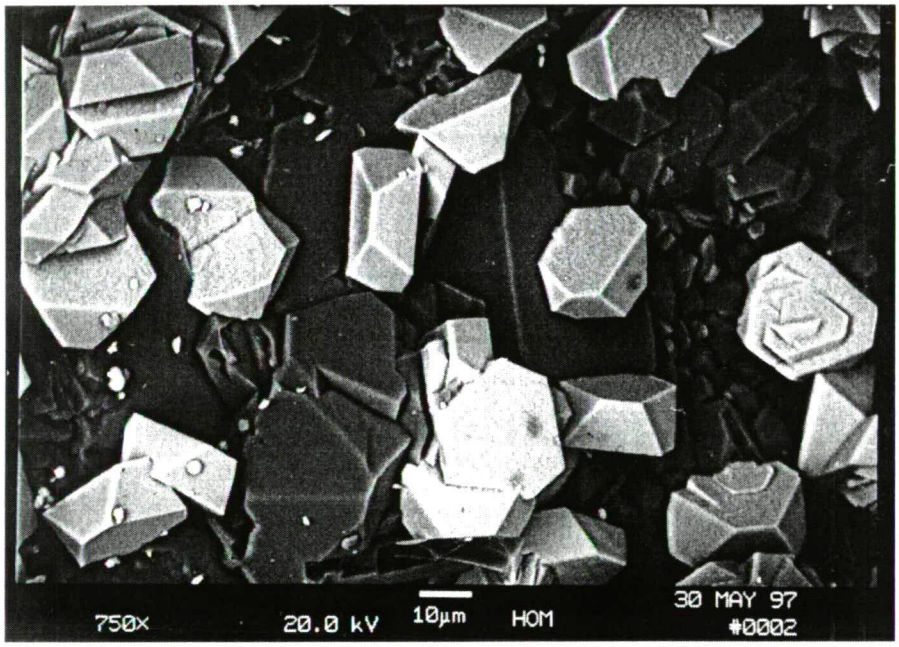

Fig. 2. Twinned plumbogummite crystals on pyromorphite (SEM photo).

Semi-quantitative chemical analyses were carried out by means of an AMRAY 1830i/T6 scanning electron microscope operated at 20kV acceleration voltage using energy-dispersive X-ray spectrometry (EDAX® VP9800 ED) at the Department of Petrology & Geochemistry, ELTE.

Quantitative chemical analyses were performed using a JEOL JXA-733 electron microprobe analyser (EMPA) equipped with three wavelength-dispersive spectrometers (WDS), in the Geochemical Research Laboratory of the Hungarian Academy of Sciences. The measurements were carried out with: 15 kV accelerating voltage, 40 nA beam current, beam defocus 10 µm diameter, 5 × 4 s counting time. Analytical lines: L_α for Pb, K_α for Al, Ca, S, Cl and P, K_β for As. The following standards were used: PbSe (synthetic) for Pb, artificial glass for Al, apatite for Ca, P and Cl, chalcopyrite for S, GaAs for As. For matrix correction conventional ZAF method was applied.

XRPD analysis was carried out by means of a Siemens D-500 diffractometer (CuK_α radiation, acceleration voltage 41 kV, beam current 40 nA) at the Department of Mineralogy, ELTE.

Analytical results

The studied specimens from the Szűzvár Mine, Pátka area are leached vuggy quartz vein fragments with 10-20 mm-sized cavities. Relict primary galena can be observed in the vugs. The mineral association found in the cavities consists of quartz, pyromorphite, cerussite, wulfenite, fluorite and plumbogummite. Plumbogummite is the less abundant among all these minerals.

Plumbogummite usually appears as a light brown earthy crust on pyromorphite, galena and on the cavity walls. XRPD analysis revealed that this crust is a mixture of plumbogummite and pyromorphite (Fig. 1). There are also colourless to white or pale brown microcrystalline crusts of plumbogummite on the surface of some pyromorphite aggregates. SEM photos proved that this crust is composed of euhedral intergrown crystallites of plumbogummite (Fig. 2).

Pyromorphite is the most abundant mineral in close association with plumbogummite. Several morphological and colour varieties are present. Two of them are the hosts to plumbogummite: a) light green, 1–3 mm long hexagonal prisms; b) brown bundle-shaped aggregates of thin needles.

Crystal morphology

SEM images of the samples show individual crystals and small aggregates of plumbogummite (Fig. 2). The size of the individual crystals is 10–20 µm, and the diameter of the aggregates is about 40–70 µm. The crystals have pseudo-octahedral tabular habit as a result of the combination of a rhombohedron and a pinacoid, the latter being dominant. Some of the crystals are penetration twins, where the twin law is a 70° rotation around [211] (Zajzon et al., 2000).

The microtexture and the relationship between plumbogummite and pyromorphite crystals were studied on back-scattered electron images of polished sections. Two different textural types of plumbogummite were distinguished:

1) Distinct euhedral, isometric, pseudo-hexagonal crystals with the size of 50–150 µm occur, as inclusions in pyromorphite. The size of single crystals is about 25–40 µm. Two sub-

types were set up according to the host pyromorphite:

1a) Pyromorphite having dark brown internal reflection under crossed polars exhibits a fibrous texture. This texture is corresponds to the 1b) micro-morphotypes of pyromorphite observed by stereo microscopy. The BSE image (Fig. 3) shows a homogeneous mass of pyromorphite (white) due to the very close packing of needles in the fibrous aggregate. Plumbogummite (dark grey) appears as isometric crystals. Minute prismatic pyromorphite inclusions are frequent in plumbogummite cores suggesting that they are individual needles on which plumbogummite is overgrown. The size of these inclusions is 2–10 μm, corresponding to the diameter of the needles (Fig. 3).

1b) The host pyromorphite is not as homogenous as it was in sub-type 1a, but contains fissures, micro-gaps. Green internal reflections can be observed in reflected light, and there is no visible fibrous texture. The shape and the habit of plumbogummite, is the same as in the previous sub-type. The only difference is the lack of pyromorphite inclusions in plumbogummite (Fig. 4).

2) Earthy, microgranular, fibrous, spongy mass (Fig. 1, dark grey). The size of the crystallites are close to 1 μm. Plumbogummite surrounds the pyromorphite mass (white) but rarely also appears as patches within. This texture suggests the alteration of pyromorphite to plumbogummite.

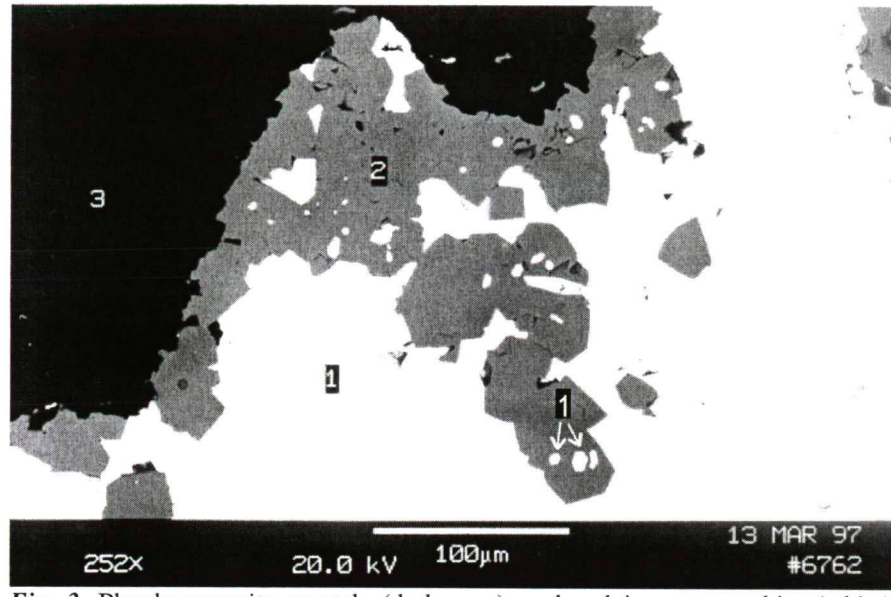

Fig. 3. Plumbogummite crystals (dark grey) enclosed in pyromorphite (white). Hexagonal sections of pyromorphite needles (white) appear as minute inclusions in the cores of plumbogummite (BSE image). 1 = pyromorphite, 2 = plumbogummite, 3 = quartz.

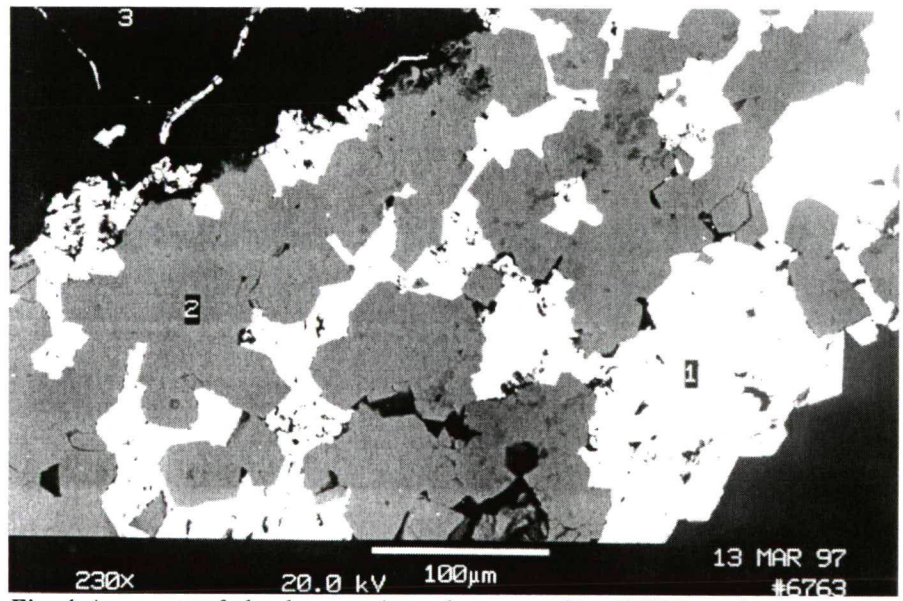

Fig. 4. Aggregate of plumbogummite and pyromorphite (BSE image). Numbers as in Fig. 3.

MICROPROBE ANALYSES

The results for plumbogummite analyses are listed in Table 1. The standard deviation of the values is small. Therefore the data can be used for the determination of the chemical formula. H_2O was calculated by the difference (13.5 wt%) from total H_2O. The amount of OH was derived using charge balance equations. The calculated formula is $Pb_{1.08}Ca_{0.02}Al_{2.93}[(OH)_{6.29}|(PO_3(OH))_{0.86}|PO_4]\times 0.98H_2O$.

X-RAY POWDER DIFFRACTION

An X-ray powder pattern (Fig. 5 and Table 3) was recorded from a plumbogummite-bearing mixture (Textural type 2, see on Fig. 5). The main component of the mixture proved to be pyromorphite, but characteristic reflections of plumbogummite can be

Table 1. Chemical composition of plumbogummite, measured by EMPA (wt%). Theoretical values are also given for comparison. Cl, S and As were below detection limit (0.05 wt% for Cl, S and 0.04 wt% for As).

analysis	PbO	Al_2O_3	CaO	P_2O_5	Σ
1.	40.84	25.01	0.25	21.67	87.77
2.	40.60	25.21	0.20	21.91	87.92
3.	39.62	24.21	0.22	21.40	85.45
4.	39.46	24.70	0.20	21.73	86.09
5.	39.00	23.94	0.29	22.05	85.28
average	39.90±0.78	24.61±0.53	0.23±0.04	21.75±0.25	86.50±1.26
theoretical	38.41	26.32	0	24.43	89.16

Table 2. Chemical composition of plumbogummite from different localities (in wt%). (The following components were also detected, but not shown on this table: Ivanhoe mine: CuO 0.92 %, SO_3 0.67 %, As_2O_5 0.04 %, Fe_2O_3 0.01 %; Roughten Gill: CO_2 3.12 %; Diamantina No. 1: SiO_2 0.70 %, CaO 0.62 %, CeO 0.16 %; Diamantina No. 2: SiO_2 0.64 %; Szűzvár mine: CaO 0.24±0.04 %).

Occurrences	References	PbO(wt%)	Al_2O_3(wt%)	P_2O_5(wt%)	H_2O(wt%)	Σ
Ivanhoe mine, Australia	Slansky, 1977	38.90	25.45	22.47	11.55	98.37
Roughten Gill, Cumberland, GB	Hartley, 1900	37.03	28.74	18.64	12.73	97.14
Diamantina, Brasilia No.1	Hussak, 1906	35.50	24.92	22.50	16.30	100.64
Diamantina, Brasilia No.2	Hussak, 1906	35.83	25.31	22.11	16.08	99.97
Synthetic	Schwab et al., 1990	37.60±0.3	24.70±0.4	25.40±0.7	11.50±0.1	99.2±1.5
Theoretical		38.41	26.32	24.42	10.85	100.00
Szüzvár mine, Velence Mts., H	This study	39.90±0.78	24.61±0.53	21.75±0.25	13.50	100.00

identified as well. An additional small peak can be attributed to the quartz gangue (separation residue); the reflections of aluminium came from the sample holder.

DISCUSSION – GENETIC ASPECTS OF PLUMBOGUMMITE

Plumbogummite usually occurs as secondary mineral in lead deposits. It can rarely be found also in low temperature hydrothermal systems as well (Weiner and Hochleitner, 1997). Rojkovič (1993) mentioned cerian plumbogummite from the supergene products of a U-REE mineralization formed in a quartz-apatite vein at Čučma (Slovakia). Baker (1964) and Förtsch (1968) pointed out the close genetic relationship of hinsdalite–plumbogummite and pyromorphite. Baker (1964) reported hinsdalite pseudomorphs after pyromorphite. Phase equilibrium studies of these minerals revealed that pyromorphite spontaneously alters to hinsdalite in a solution enriched in Al-SO_4-OH because of the lower free energy of the latter. Förtsch (1968) recognised rhythmically microlayered plumbogummite overgrown on pyromorphite. Distinct layers were built by fibrous plumbogummite by their optical *c* axes oriented perpendicularly to the prism faces of pyromorphite. The same optical relationship between plumbogummite and pyromorphite was reported from the Ivanhoe Mine, Australia (Slansky, 1977). The relation of these two minerals can be explained on structural basis by the similarity of the Pb–O distance in pyromorphite to the Al–O distance in plumbogummite (Slansky, 1977).

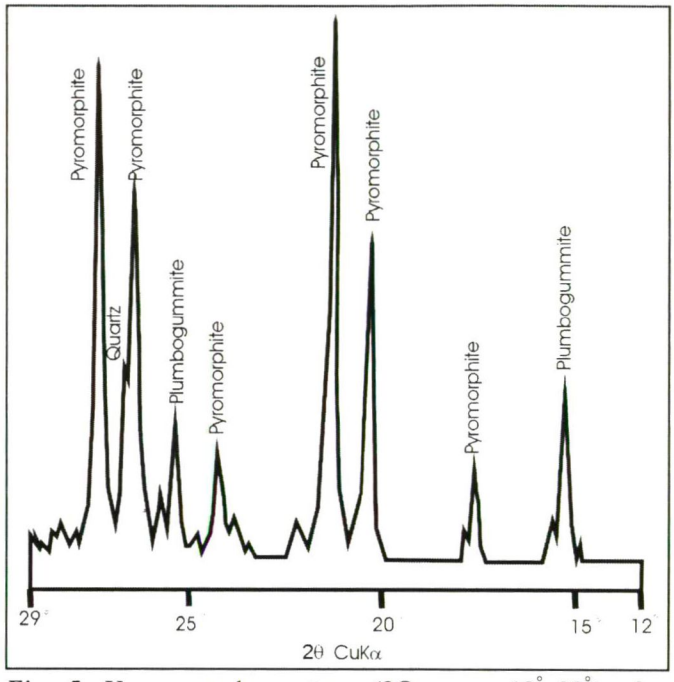

Fig. 5. X-ray powder pattern (2Θ range 12°–29°) of a plumbogummite-bearing sample.

Table 3. Evaluation chart of the X-ray powder diffraction pattern of a plumbogummite-bearing sample.

sample: 11481			*Al: ICDD 4-787, **quartz: ICDD 33-1161			pyromorphite: ICDD 19-701			plumbogummite: ICDD 35-623		
no	*d* (Å)	I/I_0	*d* (Å)	I/I_0	*hkl*	*d* (Å)	I/I_0	*hkl*	*d* (Å)	I/I_0	*hkl*
1	5.75	2							5.70	90	101
2	5.63	<1							5.57	17	003
3	5.01	1				4.99	8	101			
4	4.96	<1							4.91	16	012
5	4.34	4				4.33	20	200			
6	4.14	7				4.13	45	111			
7	4.00	<1									
8	3.74	<1				3.73	2	201			
9	3.68	1				3.67	8	002			
10	3.523	2							3.503	60	110
11	3.474	1							3.442	19	104
12	3.383	5				3.38	25	102			
13	3.361	2	**3.342	100	101						
14	3.278	6				3.27	35	210			
15	2.988	85				2.985	100	211	2.996	100	113
16	2.961	95				2.959	100	112			
									2.929	11	015

Table 3. continued

sample: 11481			*Al: ICDD 4-787, **quartz: ICDD 33-1161			pyromorphite: ICDD 19-701			plumbogummite: ICDD 35-623		
17	2.886	12				2.885	60	300	2.852	14	202
									2.785	10	006
18	2.503	<1				2.497	2	220			
19	2.468	<1							2.456	11	024
20	2.443	<1				2.440	2	212			
21	2.348	18	*2.338	100	111						
22	2.276	1							2.274	14	211
23	2.238	2				2.226	6	302	2.247	16	205
									2.222	30	107
24	2.201	3				2.195	16	113	2.212	30	122
25	2.166	1				2.162	8	400	2.181	12	116
26	2.067	6				2.063	35	222			
27	2.032	100	*2.022	47	200				2.024	5	300
28	2.010	4				2.007	18	312	2.011	10	214
29	1.986	3				1.983	10	320	1.976	6	018
30	1.962	4				1.957	20	213			
31	1.918	4				1.915	25	321	1.902	25	303
32	1.892	4				1.886	20	410	1.892	9	125
33	1.865	5				1.861	25	402	1.875	2	027
34	1.838	2				1.833	10	004			
35	1.758	<1							1.751	17	220
36	1.726	<1				1.721	2	114	1.720	3	208
37	1.692	<1				1.688	2	204			
38	1.682	1				1.678	4	412	1.676	3	131
									1.672	3	223
									1.655	6	217
									1.641	7	119
39	1.639	1				1.633	8	420	1.636	3	306
40	1.626	1				1.623	6	331			
41	1.601	1				1.599	6	214	1.611	3	101
42	1.570	1				1.564	4	502			
43	1.551	2				1.553	4	510	1.545	1	128
						1.547	8	304			
						1.540	6	323			
44	1.519	3				1.519	8	511			

PLUMBOGUMMITE FROM PÁTKA

Plumbogummite from the Szűzvár Mine is found in close association with pyromorphite. The textural relationship on Fig. 3 can be explained as plumbogummite crystals were grown on a few needles of a closely packed, bundle-shaped, fibrous pyromorphite aggregate. This fibrous morphotype of pyromorphite was also recognised by binocular and reflected light microscopy. During the growth of this aggregate plumbogummite grew simultaneously on some individual needles of pyromorphite. At the end of the formation of the fibrous aggregate the needles coalesced, enclosing some plumbogummite crystals as inclusions. The process when plumbogummite directly overgrow on pyromorphite is similar to those published by Förtsch (1968) and Slansky (1977). On Fig. 2, euhedral crystals of plumbogummite are overgrown on and intergrown with pyromorphite indicating the same relationships between the two phases. Similar texture can be recognised on Fig. 4. In this case pyromorphite and plumbogummite formed together and filled in the empty spaces. Here plumbogummite crystals are free of inclusions of pyromorphite because of the non-fibrous habit of the latter.

SEM observations made on the earthy plumbogummite crust shows a different textural relationship (Fig. 1). Here plumbogummite replaces pyromorphite, suggesting different conditions of formation, possibly supergene weathering.

In conclusion, plumbogummite and pyromorphite were formed simultaneously in equilibrium and the earthy type of plumbogummite is an alteration product of pyromorphite

At least four pyromorphite generations were found in close association with plumbogummite.

1) Brown, fibrous, bundle-shaped aggregate of pyromorphite needles (Fig. 3).

2) Light green, homogeneous, non-fibrous pyromorphite (Fig. 4).

3) Prismatic pyromorphite on which splendid twinned crystals of plumbogummite are overgrown (Fig. 2).

4) Brownish grey, earthy crust of pyromorphite and plumbogummite (Fig. 1).

The formation of plumbogummite and pyromorphite may be related to a late-stage hydrothermal event during or after the leaching of the main mass of primary ores leaving behind a penetrable cellular texture. This process may lead to the well-developed crystals of plumbogummite and pyromorphite and their close spatial association. Their textural characteristics and relation, also suggest that they have been formed at the same time, during the same supergene oxidation-cementation process. This latter origin is more probable but the former cannot be excluded either. The earthy plumbogummite crust is very likely a weathering product of pyromorphite.

Conclusions

Plumbogummite was described as a new mineral species for Hungary. Pátka-Szűzvár is the second known locality of plumbogummite in the Carpathian-Pannonian Region. According to textural characteristics and mineral paragenesis, which are similar to other occurrences cited in the literature, plumbogummite was either formed by secondary supergene processes or may be related to a late hydrothermal event.

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